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Comparison of CF_4 and SF_6 based plasmas for ECR etching of isotopically enriched ^{10}Boron films

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ABSTRACT

Isotopically enriched ^{10}boron films have been successfully etched in an ECR etching tool using CF_4 and SF_6 based plasmas. Comparisons between the two are made with regards to etch rate, selectivity to the underlying Si device structure, and morphology of the ^{10}boron post-etching. Our present film etching development is expected to be critical for the fabrication of next generation thermal neutron solid state detectors based on ^{10}boron.

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Development of solid state thermal neutron detectors to replace current helium-3 (^{3}He) gas based detectors is of interest due to the possibility of wide deployment of inexpensive and efficient detectors for special nuclear materials. Solid state detectors are expected to have lower operating voltages, smaller foot-prints, and insensitivity to microphonics compared to ^{3}He gas-based detectors. Therefore, semiconductor based detectors are one preferential choice for homeland security applications, as well as potential choices for neutron detection in selected astronomy and particle physics experiments.

Indeed, a variety of semiconductor detectors have been developed.[1-7] We have recently reported one approach that utilizes a silicon (Si) P-I-N diode pillar array structure filled with ^{10}boron.[8] Theoretical efficiencies of this device architecture has the potential to exceed 50% when the fabrication and detection parameters are optimized.[9] Fabrication of such device structures requires a suitable method to remove the top coating of ^{10}boron in order to reveal the underlying Si P-I-N structure for metallization. Towards this end, we report the development of an Electron Cyclotron Resonance (ECR) plasma etch approach based on Fluorine chemistries with CF_4 and SF_6. To the best of our knowledge, our reported ECR etching of ^{10}boron has the highest etch rates achieved for this material, to date.

Previous work to remove boron with plasmas has been reported for the purpose of cleaning thermonuclear reactor chambers, in which the Boron is used as a protective coating.[10-12] Groups have reported the use of H-, Cl-, and F-based plasmas for these purposes. Hydrogen glow discharges produce extremely low etch rates, while Chlorine based ones do not fair significantly better, with reported rates of <9 x 10^{-3} Å/s and 0.1 Å/s respectively.[11] The reaction products of these chemistries limit the etch rates, as boron hydrides are not energetically favorable while BCl_3, the likely reaction product of the Cl-based etch, is easily dissociated in a plasma.

An improvement was reported for a $CF_4/H_2/O_2$ plasma, which has a rate of 40 Å/min.[12] This is due to the very high volatility and thermodynamic favorability of the reaction by-product BF_3. The presence of O_2 was reported to be necessary in this etching process in order to prevent a build-up of carbon on the surface, deposited by the CF_4, which results in slowing and eventually halting the etch process. We have examined the use of this chemistry in an ECR. For comparison, we have also examined pure SF_6, which is expected to have a higher fluorine radical density. The expected etch reactions are

(1) $3\ CF_{4(g)} + 3\ O_{2(g)} + 4\ B_{(s)} \rightarrow 3\ CO_{2(g)} + 4\ BF_{3(g)}$

(2) $SF_{6(g)} + 2\ B_{(s)} \rightarrow 6\ S_{(s)} + 2\ BF_{3(g)}$

In fact, these are the least favorable reactions. The plasma will contain radicals and ions formed from CF_4 and SF_6, which will react more readily. In addition, by products such as BF_2 or BF could form. Removal of S from the surface is not expected to limit the second reaction, as it should be more easily sputtered from the surface during etching due to the weaker nature of the S-S bonds compared to C-C.

Samples were prepared using a multi-step lithographic and etching process. Silicon wafers are patterned with photo-resist to generate an array of squares of 2 μm sides and 2 µm inter-spacing using standard lithographic techniques. These patterned photo-resists were then etched using an STS Si Deep Reactive Ion Etcher (DRIE) to form 3-D pillars. Following this, ^{10}boron was conformally deposited by Low Pressure Chemical Vapor Deposition (LPCVD) at the University of Nebraska-Lincoln, and has previously been reported.[13] ^{10}boron filled samples were then inserted into the ECR chamber and exposed to either CF_4 or SF_6 based plasmas under several sets of conditions. Etch rates were determined by cleaving samples and measuring the ^{10}boron thickness with a scanning electron microscope (SEM) before and after each etch.

The initial experiments consisted of using both $CF_4/H_2/O_2$ and SF_6 plasmas with flow rates of 5 sccm CF_4 or SF_6, with 10 sccm H_2 and 5 sccm O_2 added for the CF_4 etch only. Pressure was maintained at 3 mTorr with an ECR source power of 850W and magnet current of 170A. RF power was varied from 0 to 500W in order to observe the effect of incident ion energy on the etch rate. Figure 1 shows SEM images of the ^{10}boron surface (a) prior to and after etching with (b) CF_4 and (c) SF_6 with an RF power of 200W. The final morphology of each etch is significantly different. For the case of CF_4, the tops of the pillars are exposed after the sides of the pillars. For SF_6, the tops are exposed first, as would be expected. In addition, the difference in the selectivity to the underlying Si is clear. It is well known the use of excess O_2 serves to decrease the etch rate of Si in F-based plasmas.[14] Because of this, the CF_4 etch leaves the pillar structure protruding above the ^{10}boron while the SF_6 creates depressed features. Figure 2 displays the etch rates under varying RF powers. For CF_4-based plasmas, an etch rate of ~0.25 µm/min was observed for most conditions above 100W. A slight etch rate increase was observed at 500W, but is within the measurement error. The B:Si etch selectivity (≈ 5:1) is very high, likely due to the inclusion of O_2 in the plasma.

SF_6-based plasmas showed significantly higher etch rates. A minimum rate of 0.25 µm/min was observed even at 0W RF, with a maximum at 0.72 µm/min. The B:Si etch selectivity is at a minimum of ~0.06 at 0W and increases to just less than 1 at 500W. From this, it is clear that a minimum amount of ion energy is necessary to enable reasonable etch rates, but beyond this has a minor effect. At very high RF powers, the etch rate in SF_6 decreases, which is likely due to sputtering of reactants from the surface before formation of etch products.

The effect of gas flow rate was also examined. Flow of both CF_4 and SF_6 were varied from 5 to 20 sccm, the maximum possible in our system. For the CF_4 etch, the ratio of H_2 and O_2 was kept constant. Figure 3 shows the results. Under varying CF_4 flows, an increase in the etch rate at 10 sccm is observed followed by a decrease at 20 sccm, with a maximum of > 0.35 µm/min. For SF_6, the etch rate increases up to 20 sccm for a maximum of > 0.9 µm/min. Increased SF_6 flow also results in a decreasedSi:B selectivity, with a minimum of 0.7 at 20 sccm SF_6. It is clear that each of these etches are dependent on the plasma chemistry and supply of reactants.

We have demonstrated ECR etching of ^{10}boron with CF_4 and SF_6 plasmas. Each possesses advantages. CF_4, while slower, is a fairly stable etch under varying conditions. In addition, the necessary use of O_2 in the plasma ensures a good deal of selectivity to underlying Si structures. SF_6 allows for a more rapid etch of ^{10}Boron and more variability of the etch rate as well as a differing profile of the final etch structure. It is expected that further refinement of the SF_6 chemistry, with the use of H_2 and O_2, will allow for significant tuning of the selectivity to Si as well as the etch rate.

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Figure 1. Typical SEM images of ^{10}Boron filled pillars (a) before etching, (b) after CF_4 etching, and (c) after SF_6 etching.

Figure 2. Etch rate vs RF power for 3 mTorr at 850W ECR Power with 5/10/5 sccm $CF_4/H_2/O_2$ and 5 sccm SF_6.

Figure 3. Etch rate dependence on CF_4 and SF_6 gas flow for 3 mTorr at 850W ECR Power and 200W RF.

Figure 1.

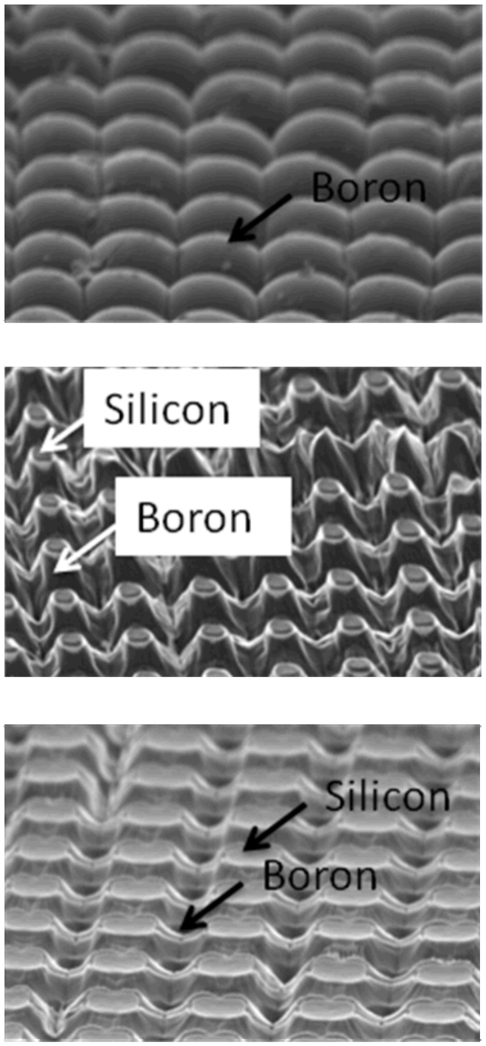

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Figure 2.

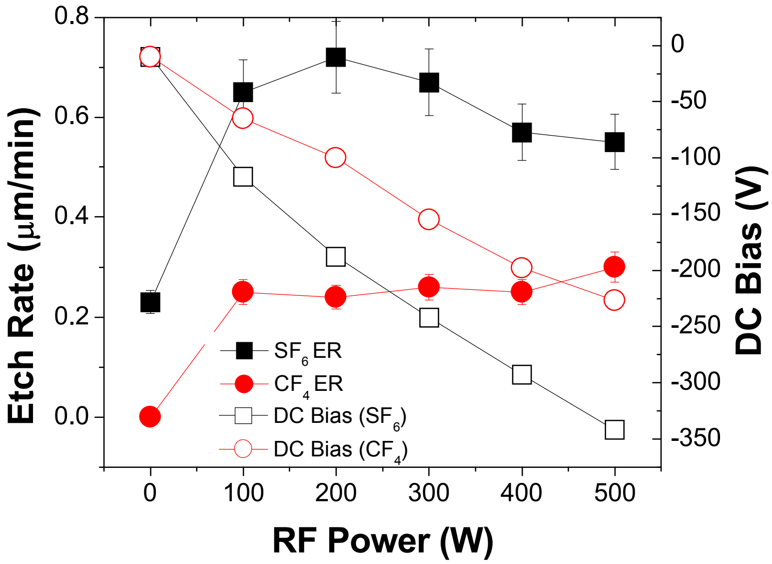

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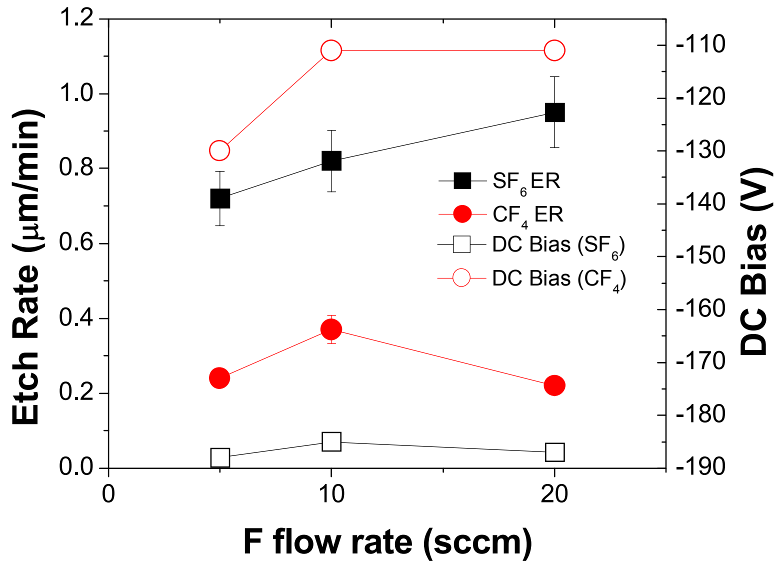
Figure 3.



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